Eur. Phys. J. D **49**, 311–315 (2008)
DOI: 10.1140/epjd/e2008-00174-3

THE EUROPEAN PHYSICAL JOURNAL D

On the transition between directed bonding and helium-like angular correlation in a modified Hooke-Calogero model

U. Müller-Herold[a]

ETH Zurich, P.O. Box CAB 24, 8092 Zurich, Switzerland

Received 18 June 2008 / Received in final form 4 August 2008
Published online 3rd October 2008 –

Abstract. Angular correlation in three-body systems varies between the limiting cases of slightly perturbed equi-distribution, as in the electronic ground state of helium and directed bond-type bent structure, as in the isolated water molecule. In an exactly solvable modification of the Hooke-Calogero model, it is shown that there is a sharp transition between the two cases if the particles' masses are suitably varied. In the Hooke-Calogero model attraction between different particles is harmonic and the repulsion between equal particles is given by a $1/r^2$ potential. The bent structure appears in the angular distribution function if the masses of the two equal particles are below a critical value, which depends on the mass of the third particle. Above the critical value, the angular correlation is of helium type and exhibits a minimum at 0° corresponding to the Coulomb hole and a maximum at 180°. The model thus demonstrates the modulating role of mass in the transition between semi-rigid structure and more diffuse nuclear states.

PACS. 33.15.Dj Interatomic distances and angles – 03.65.Ge Solutions of wave equations: bound states

1 Introduction

Directed bonding is an emerging characteristic at the molecular level without precedent in nuclear physics. In particular, this applies to the ground states of quasi-rigid molecules, which are characterized by almost fixed bond angles defined through the relative positions of three neighboring nuclei at a time. A well-known example is the V-shaped isolated water molecule where the H–O–H bond angle is 104.50° [1].

By contrast, the helium atom does not show a comparable e^-–He^{++}–e^- angle, although there is *some* angular electron correlation. This can be seen from the nearly exact ground-state wave function given by Hylleraas [2] in the early days of quantum mechanics

$$\Psi(\vec{q}_1,\vec{q}_2)=\left(1+\gamma\sqrt{(\vec{q}_1-\vec{q}_2)^2}\right)e^{-\beta(q_1+q_2)} \qquad (1)$$

where $\vec{q}_i$, $i=1,2$, are the electron coordinates, $q_i=|\vec{q}_i|$, and $\beta\in\mathbb{R}$ and $\gamma\in\mathbb{R}$ are such that they minimize the energy. The probability of finding the two electrons at a distance q from the nucleus in a shell of thickness dq is proportional to

$$dq\,q^2\,(\Psi\Psi^*)\,(\vec{q}_1,\vec{q}_2)_{q_1=q_2=q} = dq\,q^2\left(1+\gamma q\sqrt{2-2\cos\alpha}\right)^2\times e^{-4\beta q} \qquad (2)$$

where α is the included angle. Integration over q leads to the angular distribution

$$\rho_{\mathrm{He}}(\alpha)=\int_0^\infty dq\,q^2\,(\Psi\Psi^*)\,(\vec{q}_1,\vec{q}_2)_{q_1=q_2=q} = 4\beta^2+6\beta\gamma\sqrt{2-2\cos\alpha}+3\gamma^2\,(2-2\cos\alpha). \qquad (3)$$

For the optimal values [3] $\beta=1.85$ and $\gamma=0.365$, one obtains the angular probability distribution shown in Figure 1. It shows the characteristics of what we will call 'helium-like angular correlation': a minimum at $\alpha=0°$ – representing the Coulomb hole – followed by a monotonic increase and a flat maximum at $\alpha=180°$.

In comparison to helium there is no equally simple equivalent of the Hylleraas wave function for the *nuclear* dynamics in tri-atomic molecules. For small amplitude vibrations the nuclear dynamics are mostly described in rectilinear normal or local coordinates. However, using a curvilinear bending coordinate and two rectilinear stretching coordinates, Hougen et al. [4] derived an effective Hamiltonian for large-amplitude bending and solved the corresponding one-variable Schrödinger equation by numerical integration [5]. Schematically, the probability distribution for the bending coordinate of a bent molecule is shown in Figure 2.

[a] e-mail: mueller-herold@env.ethz.ch

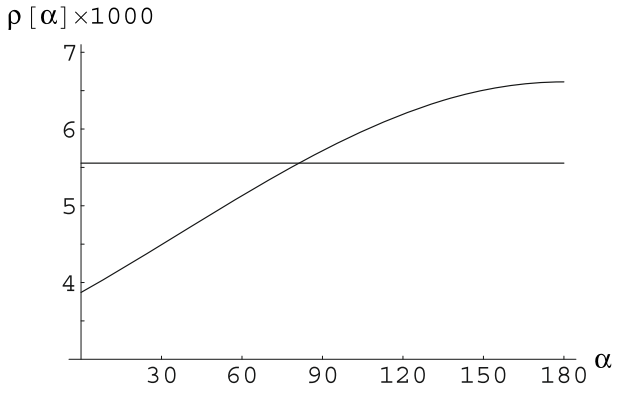

Fig. 1. Normalized distribution function of the helium inter-electron angle α [degree] as derived from the Hylleraas wave function. The straight line at 5.56 represents the $(1s)^2$ situation of Hartree-Fock-type uncorrelated wave functions.

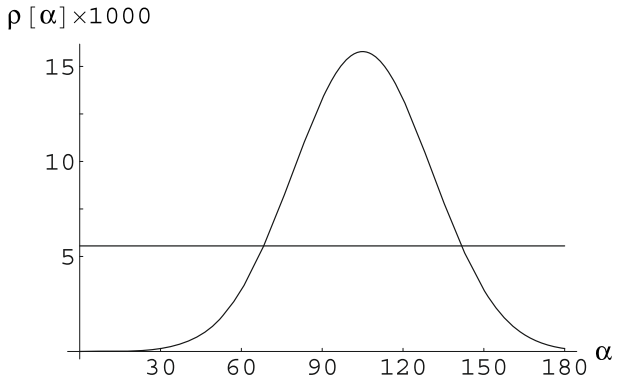

Fig. 2. Schematic normalized distribution function ρ for the bond angle α [degree] in the ground state of a bent tri-atomic molecule. Contrary to helium-like angular correlations there are *two* minima at 0° and 180° and a maximum in between (which was chosen to be at $\alpha = 104.5°$). The straight line at 5.56 again represents an uncorrelated $(1s)^2$-type situation

2 Posing the problem

The emergence of spatial structure at the molecular level still raises many questions. Historically, the first important result was the celebrated paper by Born and Oppenheimer [6] where they showed that in a perturbation treatment the full molecular Schrödinger equation reduces, in zeroth order, to the Schrödinger equation of the electrons in the electrostatic field of a classical fixed nuclear framework. As perturbation parameter they used the ratio $\varepsilon = (m_-/M_+)^{1/4}$, where m_- is the mass of the electron and M_+ is a mean nuclear mass. In such a *clamped-nuclei* description, inter-nuclear distances and angles have sharp (dispersion-free) values. Further information is provided by consideration of higher terms in the expansion: the term proportional to ε^2 describes the oscillations of the nuclear frame, as does the term ε^4 with respect to its rotation, whereas the terms proportional to ε and ε^3 vanish.

In spite of its practical success in many cases, the Born-Oppenheimer approach did not solve the problem of molecular structure, but only posed it in a formal way: since the nuclei have finite mass (i.e. $\varepsilon > 0$) the convergence properties of the perturbation series come into play if one tries to infer nuclear structure from the infinite nuclear mass limit with $\varepsilon = 0$. With regard to energy, Combes and Seiler showed that the Born-Oppenheimer approximation can be rigorously justified by singular perturbation theory [7–9]. Their result however, relates to diatomics and has never been extended to polyatomic molecules. It states that ε is the parameter of an asymptotic expansion, which in the singular limit $\varepsilon \to 0$ *creates* a qualitatively new phenomenon: molecular structure, but which does *not* converge in the relevant Hilbert space and operator topologies. This implies that the Born-Oppenheimer procedure definitely does not work for *all* other observables even if it converges for energy. The particular question of whether it works for molecular structure was raised in a widely perceived paper by Woolley [10], who essentially answered it in the negative.

However, for small molecules whose Born-Oppenheimer ground state shows a quasi-rigid behavior, some reverberations of molecular structure should be retrievable from a fully quantum mechanical wave function, i.e. without clamping the nuclei in a first approximation step (for an overview see Refs. [11,12]). In this spirit, the present author [13] recently demonstrated the unfolding of a rotating dumbbell-like proton distribution from an $(1s)^2$-type electron distribution through variation of masses in the fully quantum mechanical Hooke-Calogero Hamiltonian for H^- and H_2^+. The dumbbell-like molecular structure appears as an expression of increasing spatial correlation due to increasing mass of the two equal particles during the passage from H^- to H_2^+. For large values of the equal masses it approaches a form similar to its Born-Oppenheimer counterpart.

It is the objective of the present paper to do a similar analysis for bond angles and to investigate the transition from helium-like to bent H_2O-type angular correlation in a modified Hooke-Calogero model, again through variation of the masses. The analogue of a bond angle is equated with the maximum of an angular probability distribution, which is calculated from the pair correlation function obtained as the ground-state expectation value of the two-density operator. As a result, mass is found to be a dominant modulating factor in the transition from semi-rigidity to more diffuse nuclear configurations. Surprisingly, it turns out that there is a sharp and well-defined transition line between these two qualitatively different manifestations of spatial structure in molecular systems.

3 A modified Hooke-Calogero Hamiltonian and its decoupling

Harmonium (or Hooke's law atom) is a three-body model where two equal particles interact with a third, different one through harmonic potentials whereas the repulsion between the two equal particles is Coulombic [14]. Although the Coulombic helium and its harmonium counterpart are

quantitatively different – harmonium being a more diffuse species, and the overlap of two ground-state wave functions being about 0.6 – meaningful qualitative comparisons can be made between the two [3].

If, in addition, Coulombic repulsion is replaced by an inverse square potential, one arrives at a class of exactly solvable three-body models usually associated with the name of Calogero, who introduced them for one-dimensional systems [15]. In the 1980s this so-called Hooke-Calogero model was adapted to three dimensions by Makarewicz [16]. Recently, it was extended by Lopez et al. [17] to four particles in order to obtain an analytical closed-form non-Born-Oppenheimer wave function for the H_2 molecule. Again, it was observed that the analysis of the Coulomb holes for the electrons reveals a remarkable similarity of the model electron correlation effects as compared to real Coulombic systems. This makes it promising to further explore Hooke-Calogero-type models in the study of qualitative features of Coulombic few-body systems.

In atomic units, the *modified* Hooke-Calogero Hamiltonian is defined

$$\hat{H} = -\frac{1}{2m_e}\Delta_{\vec{Q}_1} - \frac{1}{2m_e}\Delta_{\vec{Q}_2} - \frac{1}{2m_u}\Delta_{\vec{Q}_3} + V \tag{4}$$

$$V = \frac{1}{2}\left(\vec{Q}_3 - \vec{Q}_1\right)^2 + \frac{1}{2}\left(\vec{Q}_3 - \vec{Q}_2\right)^2 + \frac{1}{(\vec{Q}_2 - \vec{Q}_1)^2} + \frac{g}{4}\left(\vec{Q}_2 - \vec{Q}_1\right)^2 \tag{5}$$

where $\vec{Q}_1$, $\vec{Q}_2$ and m_e are the coordinates and the mass of the two equal particles, $\vec{Q}_3$ and m_u are the coordinates and the mass of the third "unequal" particle. The fourth term with $g > 0$ represents the modification with respect to the original Hooke-Calogero model [12]. In Jacobi coordinates

$$\begin{pmatrix} \vec{r}_1 \\ \vec{r}_2 \\ \vec{r}_3 \end{pmatrix} = \begin{pmatrix} -1 & 1 & 0 \\ -1/2 & -1/2 & 1 \\ m_e/M & m_e/M & m_u/M \end{pmatrix} \begin{pmatrix} \vec{Q}_1 \\ \vec{Q}_2 \\ \vec{Q}_3 \end{pmatrix} \tag{6}$$

the Hamiltonian reads

$$\hat{H} = -\frac{1}{m_e}\Delta_{\vec{r}_1} - \frac{1}{2\mu}\Delta_{\vec{r}_2} - \frac{1}{2M}\Delta_{\vec{r}_3} + \frac{1+g}{4}\vec{r}_1^{\,2} + \frac{1}{\vec{r}_1^{\,2}} + \vec{r}_2^{\,2} \tag{7}$$

where $M = 2m_e + m_u$ denotes the total mass and $\mu = 2m_e m_u/(2m_e + m_u)$ is the reduced mass of the three-body system. The Hamiltonian, accordingly, separates into three commuting parts:

$$\hat{H}_1 = -\frac{1}{m_e}\Delta_{\vec{r}_1} + \frac{1+g}{4}\vec{r}_1^{\,2} + \frac{1}{\vec{r}_1^{\,2}} \tag{8}$$

$$\hat{H}_2 = -\frac{1}{2\mu}\Delta_{\vec{r}_2} + \vec{r}_2^{\,2} \tag{9}$$

$$\hat{H}_3 = -\frac{1}{2M}\Delta_{\vec{r}_3}. \tag{10}$$

Subtraction of the center-of-mass Hamiltonian $\hat{H}_3$ then leads to the internal Hamiltonian $\hat{H}' = \hat{H} - \hat{H}_3 = \hat{H}_1 + \hat{H}_2$.

In Jacobi coordinates the harmonic coupling of the equal particles to the unequal one leads to an effective harmonic attraction between the equal particles due to the second term in $\hat{H}_1$ (with $g = 0$), which counterbalances the $1/r^2$ repulsion and gives rise to a potential minimum at $r_1 = \sqrt{2}$. For $g > 0$ the attraction is enhanced and the minimum is shifted towards smaller values of r_1.

The non-normalized ground state solutions of equations (8) and (9) are given by

$$\begin{aligned} \Psi_{1,0}(r_1) &= r_1^t e^{-\sqrt{m_e(1+g)/4}\, r_1^2/2} \\ \Psi_{2,0}(r_2) &= e^{-\sqrt{4\mu'}\, r_2^2/2} \end{aligned} \tag{11}$$

with

$$t(t+1) := m_e,\ r_i := |\vec{r}_i|,\ i = 1, 2,\ \mu' := \mu/2 \tag{12}$$

and corresponding density distribution

$$\begin{aligned} (\Psi\Psi^*)(\vec{r}_1, \vec{r}_2) :&= \left(\Psi_{1,0}\Psi^*_{1,0}\right)(\vec{r}_1)\left(\Psi_{2,0}\Psi^*_{2,0}\right)(\vec{r}_2) \\ &\propto |r_1|^{2t} e^{-\sqrt{m_e(1+g)}\, r_1^2/2}\, e^{-2\sqrt{\mu'}\, r_2^2} \end{aligned} \tag{13}$$

where the use of the proportional sign ($\propto$) allows unnecessary factors to be omitted.

4 The angular probability distribution

The angle between the three particles corresponding to a "bond angle" is the angle included by the vectors $\vec{Q}_3 - \vec{Q}_1$ and $\vec{Q}_3 - \vec{Q}_2$. The probability that $\vec{Q}_3 - \vec{Q}_1 = \vec{q}_1$ and $\vec{Q}_3 - \vec{Q}_2 = \vec{q}_2$ is the expectation value of the two-density operator

$$\begin{aligned} \hat{\rho}'(\vec{q}_1, \vec{q}_2) &= \delta(\vec{Q}_3 - \vec{Q}_1 - \vec{q}_1)\,\delta(\vec{Q}_3 - \vec{Q}_2 - \vec{q}_2) \\ &= \delta(\vec{r}_2 - \vec{r}_1/2 - \vec{q}_1)\,\delta(\vec{r}_2 + \vec{r}_1/2 - \vec{q}_2) \end{aligned} \tag{14}$$

and reads

$$\begin{aligned} \rho'(\vec{q}_1, \vec{q}_2) &\propto \int_{\mathbb{R}^3} d^3r_1 \int_{\mathbb{R}^3} d^3r_2\, (\Psi\Psi*)(\vec{r}_1, \vec{r}_2)\delta(\vec{r}_2 - \vec{r}_1/2 - \vec{q}_1) \\ &\quad \times \delta(\vec{r}_2 + \vec{r}_1/2 - \vec{q}_2) \\ &\propto |\vec{q}_1 - \vec{q}_2|^{2t}\, e^{-a(\vec{q}_1 - \vec{q}_2)^2/2}\, e^{-b(\vec{q}_1 + \vec{q}_2)^2/2} \end{aligned} \tag{15}$$

with

$$a := \sqrt{m_e(1+g)},\ b := \sqrt{\mu'} = \sqrt{m_e m_u/(2m_e + m_u)}. \tag{16}$$

The probability of finding the two equal particles at a distance q from the unequal particle in a shell of thickness dq, is proportional to

$$\begin{aligned} dq\, q^2 \rho'(\vec{q}_1, \vec{q}_2)_{q_1 = q_2 = q} &= dq\, q^{2t+2}(2 - 2\cos\alpha)^t e^{-a\, q^2(1-\cos\alpha)} \\ &\quad \times e^{-b\, q^2(1+\cos\alpha)}. \end{aligned} \tag{17}$$

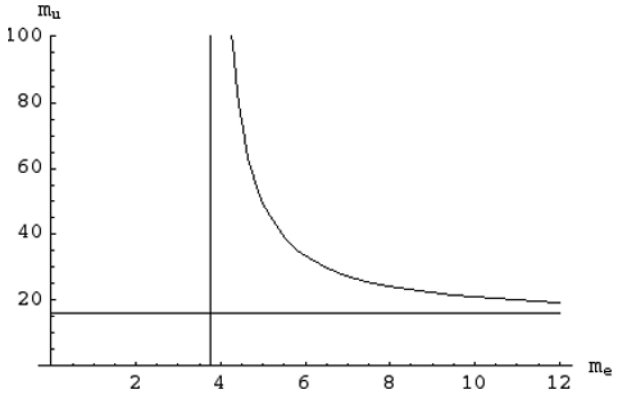

Fig. 3. Topological transition of angular correlation in the modified Hooke-Calogero model according to equation (20). The two equal particles have mass m_e and the third particle is of mass m_u. The graph of $m_{u_{krit}}$ separates helium-like angular correlation (on the right) from bent structure (on the left) for g =3 (see Eq. (5)). The lines parallel to the m_u axis and the m_e axis resp. denote the minimal values of 15/4 for m_e and 15.94 for m_u for which the transition occurs. For values of m_e smaller than 15/4 and of m_u smaller than 15.94 the structure is always bent regardless of the magnitude of the respective other mass.

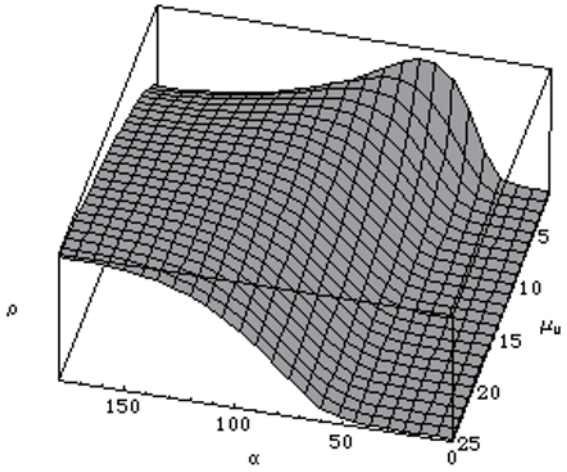

Fig. 4. Transition from helium-like angular correlation at $m_u = 25$ to bent structure at $m_u = 1$ for fixed $m_e = 100$ and $g = 3$. According to equation (20) the transition occurs at $m_u = 16.03$. At $m_u = 1$ the bond angle corresponding to the maximum of ρ is at $\alpha = 57.56°$

As in equation (3) integration over q then leads to the angular distribution

$$\rho(\alpha) \propto \int_0^\infty dq\, q^2 \rho'(\vec{q}_1, \vec{q}_2)_{q_1=q_2=q} = \frac{(1-\cos\alpha)^t}{(a(1-\cos\alpha)+b(1+\cos\alpha))^{t+3/2}}. \quad (18)$$

The distribution (18) has two extremal values at $\alpha = 0°$ and $\alpha = 180°$ third extremal value – corresponding to a bent structure if it is a maximum – can be found at

$$\cos\alpha = 1 - \frac{4}{3}\frac{t}{a/b - 1}. \quad (19)$$

For real α the cosine is restricted to $-1 < \cos\alpha < 1$. The condition $\cos\alpha < 1$ entails $1 + g > m_u/(2m_e + m_u)$. In the case that the unequal particle has large mass ($m_u \to \infty$), this entails $g > 0$ which shows that the last term in Hamiltonian (5) is instrumental for bent ground state configurations. The other condition $\cos\alpha > -1$ implies

$$m_u < \frac{(9/4)\{1+g\}2m_e}{(\sqrt{m_e + 1/4} + 1)^2 - (9/4)\{1+g\}} := m_{u_{krit}} \quad (20)$$

which for $g = 3$ is depicted in Figure 3. Equation (20) contains the main result: for masses m_u smaller than $m_{u_{krit}}$ one obtains bent structure and for m_u greater than $m_{u_{krit}}$ one obtains helium-like angular correlation. It is interesting that for values of m_e smaller than 15/4 and for values of m_u smaller than 15.94, the structure is always a bent one regardless of the value of the other mass (see Fig. 3). Furthermore, it appears remarkable that the bent "molecular" structure dominates if at least one of the masses is small (!) whereas the helium-like "atomic" situation unfolds if both masses are sufficiently large.

In order to illustrate the transition from helium-like angular correlation to bent "molecular" structure we consider fixed values of $m_e = 100$ and $g = 3$. It follows from equation (20) that for values of m_u greater than 16.03 there is a helium-like correlation with a minimum at $\alpha = 0°$ and a maximum at $\alpha = 180°$ (Fig. 4). However, for values of m_u smaller than 16.03 there is a bent structure due to an intermediate maximum of the angular distribution function. It can be seen from Figure 4 that the "bond angle" decreases with decreasing mass of m_u from 180° at $m_u = 16.03$ to 57.56° at $m_u = 1$ and that the maximum becomes more and more pronounced.

In a parsimonious interpretation equation (20) simply describes a continuous change and a qualitative difference between two limiting types of angular correlation known from He and H_2O. The potential V in equation (5) can be regarded as a potential energy surface for the dynamics of three nuclei. Usually, these energy surfaces are computed pointwise through clamped nuclei techniques. By contrast, in the present model, the potential energy is given by central force laws allowing for analytical treatment.

5 Concluding remarks

In the electronic ground states of quasi-rigid molecules the various equilibrium arrangements of the nuclei roughly coincide with local minima of a nuclear potential energy surface. This is the basis of isomerism and it may suggest that the potential generally determines a molecule's nuclear configuration. However, this does not apply to non-rigid molecules, the most famous example being the true ground state of ammonia, which is essentially a superposition of two pyramidal configurations.

In contrast to so-called "realistic" models for concrete molecules the modified harmonium can be seen as a conceptual model illustrating the fundamental behavior of three particle systems: for the *fixed* inter-particle potential given by equation (5) variation of the masses can produce a range of angular probability densities, that encompass both the non-rigid helium-like case and the quasi-rigid water-like case. It thus unveils the role of mass as a shaping factor. In the domain of Coulombic systems a related question concerning ammonia would be at what mass of H, D, and T the ground state of NHDT would turn into a pyramidal quasi-rigid chiral molecule.

The author is indebted to H. Atmanspacher (Freiburg, Germany) for critical questions and helpful suggestions.

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